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(54) GAS GENERATING COMPOSITIONS

(71) We, PYRODEX CORPORATION, a corporation organised under the laws of the State of Washington, U.S.A. of P.O.B.2905, Shawnee Mission, State of Kansas, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to propellants useful in the art of firearms, munitions, and pyrotechnics, and particularly relates to gas-forming, deflagrating compositions and methods for their production.

Black powder is the name applied to deflagrating compositions consisting essentially of an intimate mixture of potassium nitrate, sulfur and charcoal in the approximate proportions 75:10:15. Other than minor variations which have been made to produce certain desired effects, this general composition has not changed since about 1560. Black powder has largely been replaced by smokeless powder as a propellant for firearms ammunition, primarily because the latter is safer to handle and store and does not produce "fouling" or corrosion of the firearm which are both characteristic of black powder. However, the gas pressures produced by the burning of smokeless powders are many times greater than those produced by black powder, and as a result, smokeless powder requires a considerably stronger firearm and also much more care in the amount of propellant used in order that dangerous pressure levels are not produced.

The art has long sought a deflagrating propellant composition which combines the low pressure characteristics of black powder and the safe handling and storage properties of smokeless powder.

A further undesirable characteristic of black powder is the composition of its combustion products. A desirable propellant yields a very high percentage of low-molecular weight gases in its combustion products in order to impart the most efficient propulsion to a projectile. Upon combustion, black powder characteristically produces about 43 per cent of gas, 56 per cent of solids, and about one per cent of water vapor. The large amount of solid combustion products results in poor efficiency and in the copious quantities of smoke which is characteristic of black powder. The combustion products of smokeless powder, on the other hand, are almost entirely gases which are useful for efficient propulsion.

Yet another disadvantage of black powder resides in the extremely heavy and expensive equipment required in its manufacture. Thus, the composition is commonly mixed, milled under massive stone wheels, pressed in a hydraulic press at about 1200 p.s.i., granulated by crushing the presscake, and then polished and graded. The multi-step operation requires not only considerable expense in investment for equipment, but also it is time-consuming and extremely dangerous in its operation. Thus, the art is in need of a simpler, less expensive, and safer method to produce deflagrating compositions of the lower-pressure, or "black powder" type.

An important characteristic of propellants which determines their usefulness in the firearms art (including small arms, artillery, and kindred military weapons) is its rate of burning. The U.S. Army Ordnance Corps has shown that such propellants are required to burn rather slowly in order not to produce excessive pressures in the bore of a gun. The pressure must be sufficient to impart desirable velocity to the projectile and not drop too rapidly as the projectile travels towards the muzzle.

The advantage offered by our compositions is their unique property of imparting high

velocity to a projectile within a firearm or the like without the concomitant development of dangerously high pressure within the chamber. It is known in the art that the muzzle velocity of a bullet or similar projectile leaving the barrel of a firearm is proportional not to the peak pressure developed within the bore, but rather to the integrated area under the pressure-time curve. [See "Modern Pressure Measuring" by Dan Pawlak, HANDLOADER Magazine, Volume 9, Number 6 (1974) pp 26 ff.].

Although the art has long sought propellant compositions which impart high velocities without the high pressure characteristic of smokeless powder, no commercially acceptable substitute for the well-knon "black powder", without its inherent disadvantages discussed above, has heretofore been found.

It is an object of the present invention to provide gas producing deflagrating compositions useful for producing propulsion to projectiles for use in firearms, munitions, and pyrotechnics, which are safe to handle and manufacture and produce efficient propulsion to projectiles and also tend to produce high projectile velocities with low pressures.

The present invention relates to a gas generating composition for producing controlled gas pressures which comprises a substantially homogeneous mixture of (a) 30-82.5 parts by weight of an oxygen-containing oxidizing agent, (b) 14.5-45 parts by weight of an organic carboxylic acid or oxidizable derivative thereof, and (c) 1.0 to 25.0 parts by weight of water.

The oxidizing agent is generally one of a large number of oxygen-containing organic or inorganic compounds which tend to cause the rapid oxidation or deflagration of a fuel or reducing agent without the requirement of the presence of oxygen from the atmosphere. Preferred oxygen-containing oxidizing agents are solid materials at ambient temperatures, but as will be seen in the disclosure below, the solid state is not a requirement of the gas-forming mixtures of our invention. Thus, even liquid oxidizing agents are operable in our invention.

Examples of suitable oxygen-containing oxidizing agents include inorganic nitrates, such as ammonium nitrate; the alkali metal nitrates, for example, sodium nitrate, potassium nitrate; the alkaline earth nitrates, for example, calcium nitrate, barium nitrate; heavy metal nitrates, for example, lead nitrate, ferric nitrate, cupric nitrate; organic nitrates, for example, urea nitrate, quanidine nitrate; inorganic perchlorates, such as ammonium perchlorate; alkali metal perchlorates, for example, potassium perchlorate, sodium perchlorate, lithium perchlorate; alkaline earth perchlorates, for example, calcium perchlorate, magnesium perchlorate, barium perchlorate; heavy metal perchlorates, for example, lead perchlorate, ferrous perchlorate, cupric perchlorate, cobaltous perchlorate; inorganic chlorates, for example, ammonium chlorate; alkali metal chlorates, for example, sodium chlorate, potassium chlorate, lithium chlorate; alkaline earth chlorates, for example, calcium chlorate, magnesium chlorate; heavy metal chlorates, for example, cupric chlorate, lead chlorate; alkali metal permanganates, for example, ammonium permanganate; alkali metal permanganates, for example, sodium permanganate, potassium permanganate, and lithium permanganate; alkaline earth permanganates, for example, calcium permanganate, magnesium permanganate, and barium permanganate, and other metallic permanganates, for example, aluminum permanganate.

Particularly preferred oxidizing agents useful in the compositions of our invention are ammonium perchlorate, the alkali metal perchlorates, for example, sodium perchlorate, potassium perchlorate, and lithium perchlorate; ammonium nitrate and the alkali metal nitrates, for example, sodium nitrate, potassium nitrate, and lithium nitrate. These materials are readily available, are relatively inexpensive, and are comparatively stable and safe to handle. The composition preferably comprises 80-50% by weight of potassium perchlorate.

The organic carboxylic acid or oxidizable derivative thereof may be aliphatic, aromatic, heterocyclic, cyclo-aliphatic, saturated or unsaturated carboxylic acid, R-COOH or oxidizable derivative thereof wherein R is a monovalent organic radical which may be straight- or branched- chain aliphatic of from two to six carbon atoms and which may be saturated or unsaturated; aromatic having from one to three carbocyclic or heterocyclic aromatic rings, preferably of five or six members in each ring; or cyclo-aliphatic which may be fully saturated or unsaturated and may contain heteroatoms.

Where R in the above formula is aromatic the aromatic ring or rings may be unsubstituted or substituted by from one to four substituents which may be positioned in any of the available positions in the ring or rings relative to the carboxylic acid group or derivative thereof. Examples of substituents on said rings included within our invention include, but are not limited to, lower alkyl of from one to three carbon atoms, for example, methyl, ethyl, propyl; hydroxy; amino, substituted amino, including one or two lower alkyl and monocyclic aryl substituents; carboxy, nitro, lower-alkoxy of from one to three carbon atoms, nitroso.

Examples of the above described carboxylic acid, R-COOH, from which suitable derivatives may be derived, include, but are not limited to, benzoic acid, salicyclic acid, anthranilic acid, *p*-nitrobenzoic acid, *m*-toluic acid, *p*-ethylbenzoic acid, vanillic acid, resorcyclic acid, α-naphthoic acid, 3-hydroxy-2-naphthoic acid, 1-phenanthroic acid, 1,8-naphthalenedicarboxylic acid, phthalic acid, isophthalic acid, and terephthalic acid; acetic acid, propionic acid, n-butyric acid, caproic acid, isovaleric acid, 2-butenoic acid, maleic acid, succinic acid, glycine, lactic acid, phenylglycine, cyclohexanecarboxylic acid, 4-methylcyclohexanecarboxylic acid, cyclopentanecarboxylic acid, citric acid, tartaric acid, tartronic acid, and malonic acid.

Oxidizable derivatives of said organic carboxylic acids are compounds wherein the acidic function of the carboxylic acid functional group has been replaced by another functional group which does not interfere with the oxidizable properties of the molecule as a whole. We have found that a wide range of derivatives are useful for the purpose of our invention; for example, ammonium and metallic salts of said carboxylic acids, amides, esters (particularly but not necessarily, solid esters), hydroxamic acids, anhydrides, hydrazides, all of which may be unsubstituted or substituted where applicable.

Surprisingly, it has been found that especially useful derivatives of said oxidizable carboxylic acids are the ammonium and metallic salts thereof. Said salts are ordinarily stable solids which are either commercially available or are easily prepared by known methods.

Particularly preferred salts of said carboxylic acids are the ammonium and alkali metallic salts of aromatic carboxylic acids as above defined. For example, ammonium benzoate, sodium benzoate, potassium benzoate, sodium salicylate, potassium salicylate, lithium *p*-hydroxybenzoate, potassium anthranilate, ammonium *m*-nitrobenzoate, disodium phthalate are especially useful fuels for the deflagrating compositions of our invention.

An especially preferred oxidizable carboxylic acid derivative of our invention is sodium benzoate, which is readily available, is inexpensive, and produces excellent results in our compositions, as described below. Sodium benzoate also presents the added advantage that it is a corrosion inhibitor for ferrous metals, and this imparts corrosion-inhibitive action to the composition of our invention. The composition preferably comprises about 45% of potassium nitrate, 9% of charcoal, 6% of sulfur, 19% of potassium perchlorate, 11% of sodium benzoate, 6% of dicyanamide and from 1 to 4% of water, the percentages being by weight.

Another aspect of our invention comprises a mixture of the above described composition in intimate combination with proportions of black powder, i.e., about 75 parts of potassium nitrate, about 10 parts of sulfur, and about 15 parts of charcoal, all parts being by weight. We have found, surprisingly, that a range of mixtures of said ingredients from 20 per cent to 50 per cent by weight of the composition of the invention and from 50 to 80 per cent by weight of the ingredients of ordinary black powder produce a gas producing deflagrating composition with significantly improved burning properties over those of black powder *per se*. The improvement is all the more surprising because of the presence of relatively large amounts of water in the composition, which heretofore has been found to be detrimental to black powder alone.

One can prepare gas-producing deflagrating compositions of the present invention by (a) intimately mixing an oxygen-containing oxidizing component and an organic carboxylic acid or oxidizable derivative thereof with sufficient water to produce an intimate blendable mass, and (b) removing water until the water content of the mixture is from 1.0 to 25 per cent by weight depending on the end use. By employing sufficient water in the first step of this process the ingredients can be intimately blended in readily available equipment which are well known to the blending arts, for example ribbon blender, sigma-blade dough mixers, and tumble blenders.

The second step of the above process is carried out by drying means, i.e., by the application of heat, by passing dry air over the blended materials, by applying vacuum to the blended materials, or by a combination of any of the foregoing.

In the above process one can include in (a), mixed with the other ingredients, the components for ordinary black powder, namely potassium nitrate, powdered charcoal, and sulfur, and in (b) remove water until the water content of the mixture is from 0.6 to 6.0 per cent by weight.

In addition, to the above-named components as requisites in the compositions of our invention, there may also be incorporated therein the various adjuvants known to the art of propellants for their modifying the cohesiveness of the particles, the surface characteristics and the ballistic characteristics as may be desired. Examples of such adjuvants which may be incorporated in the compositions of our invention include binders, for example, dextrine, gum arabic, hydroxymethyl cellulose, hydroxyethyl cellulose hydroxypropyl cellulose, gum tragacanth, red gum (acaroid resin), and guar gum; stabilizers, for example,

diphenylamine, diethyldiphenylurea (Centralite I), N,N-diphenylurea, diphenylurethane, and 2-nitrodiphenylurea; coolants, for example, nitroguanidine, potassium bitartrate, sodium bicarbonate, hydrocellulose, anthracene, starch,. and dibutylphthalate; chemicals which can produce additional water in the combustion products, for example, sucrose, polyvinyl alcohol, paraformaldehyde, sodium borate, urea, urea nitrate, guanidine carbonate, and melamine, which can provide hydrogen or oxygen or both during the oxidation process; and catalysts known to the art, for example, sulfur, copper chromite, ferric oxide, and copper phthalocyanine.

It will be apparent to one skilled in the art that a particularly striking feature of our invention is the requirement of the presence of water as a component of our deflagrating composition. The prior art teaches that water is deleterious both to black and smokeless powder. Certain blasting or explosive compositions are known, such as taught, for example, in United States Pat. 3,449,181, which comprise an aqueous slurry of an oxidizing agent containing organic fuels. However, the compositions provided by this invention are not explosives; that is, they do not detonate, but rather burn in conformance with the term "deflagrating".

Water has also been found to sensitize certain explosive mixtures employing inorganic oxidizing agents in the presence of aluminum metal, as disclosed in United States Pat. 3,366,053.

It is not fully understood why water is essential in our compositions, but it has been demonstrated that removal of water from the compositions renders them useless for the purposes of the invention. For example, removal of water from the compositions causes the pressure to "spike"; that is, to produce high pressure immediately upon ignition which is undesirable in a propellant composition. Thus, the presence of water in compositions has been demonstrated to control the burning rate, while acting as a coolant and also providing water vapor which acts as an effective propulsive gas. It is believed that the unique thermodynamic properties of water render it ideally suited for the purposes accomplished. Moreover, the use of water in the manufacture of our compositions renders the process much safer and simpler than otherwise attainable. For example, in the presence of the ionic salts representing the oxygen-containing oxidizing agents, the water component is a good electrolyte, thus decreasing substantially the charges of dangerous electrostatic charges building up.

The compositions of our invention are useful as gas-forming deflagrating materials; that is, when ignited under conditions of controlled confinement, they burn rapidly and without detonation to produce large quantities of gaseous by-products. Thus, the compositions are useful as propellants for firearms and firearms ammunition, for military munitions, for example, in cannon, mortars, and rockets, for igniters and fuses, and for pyrotechnic devices requiring a propelling force.

The following Examples serve to illustrate our invention without limiting it thereto. In each Example parts are given as parts by weight.

Example 1

In a laboratory model tumble blender were placed 45 parts of finely-divided potassium nitrate, nine parts of powdered hardwood charcoal, six parts of powdered sulfur, 19 parts of potassium perchlorate, 11 parts of sodium benzoate, six parts of dicyandiamide, and four parts of dextrine. The blender was rotated to thoroughly mix the ingredients, and then 12 parts of water were added as a spray while the materials were being continually tumbled. The charge was tumbled for five minutes, and then stopped, and 0.5 part of micronized N,N'-ethylene-bis-stearamide wax, and 0.5 part of graphite were added. The tumbling action was again start and continued for 15 minutes. The charge was then removed and air dried at 150°F. until the moisture on an Ohaus Moisture Determining Balance (Model #6100-00) indicated that the total moisture content was 1.0 per cent. The product was screened through standard screens and that portion which passed through 14 mesh (U.S. standard sieve size) and not through 40 mesh screens was retained.

Testing Data

The burning characteristics of above-described deflagrating composition were determined by firing the composition in a specially adapted rifle firmly secured at the breech and fitted with a pressure transducer fitted into the back of the chamber. The transducer output was connected to a storage oscilloscope. A pressure-time curve was displayed on the cathode ray tube as shown as curve A in Figure 1, where pressure is read as the ordinate (X) and time as the abscissa (Y).

A charge of 80 grains of the composition described in this Example was fired with a percussion cap primer. The peak pressure reading was found to be 7837 psi gauge for an average of 10 firings. In a parallel experiment, commercial black powder (FFFg grade)

(Curve B in Figure 1) gave a peak pressure reading of 10,868 psi gauge for an average of 10 firings for an identical weight of powder.

The "muzzle velocity" of the bullet fired in each case was simultaneously measured by an electronic chronograph beginning at five feet from the muzzle of the barrel. The composition of Example 1 imparted an average velocity of 1795 feet per second (fps) to a 176 grain lead bullet, and the commercial black powder imparted an average velocity of 1657 fps to the same weight bullet.

Example 2

A propellant composed of 60 parts of potassium perchlorate, 40 parts of sodium propionate, 10 parts sulfur, five parts dextrine, and 10 parts of water was granulated in a rotating coating pan and was dried to 4.3% water content. Tests carried out as described above showed that this composition gave a peak pressure of 10,500 psi gauge and a muzzle velocity of 1494 fps.

Example 3

A composition comprising 70 parts by weight of potassium perchlorate, 30 parts by weight of sodium benzoate and the following % by weight of water gave ballistic results as indicated in the following table:

% H_2O	*Peak Pressure p.s.i. gauge*	*Time to Peak Pressure in microseconds*	*Muzzle Velocity in feet/second*
2%	25,000	100	1650
5%	18,000	100	1700
10%	10,000	100	1577
15%	7,000	800	1310
25%	2,500	2000	1231

All loadings were in a .222 commercial cartridge with a 53 grain bullet. At 25% water, the mixture is a slurry.

Examples 4-8

In a similar manner, compositions having the proportions by weight shown in Table I were prepared and found to have satisfactory deflagration properties in accordance with the invention:

TABLE I

Example No.	*Reducing Agent*	*Parts*	*Parts of $KClO_4$*	*Parts of H_2O*
4	Benzoic acid	20	80	2
5	Sucrose benzoate	20	75	2
6	Lithium benzoate	45	55	5
7	Calcium benzoate	40	60	4
8	Isatoic anhydride	25	75	2

Example 9

In a similar manner, a composition prepared by blending 75 parts of potassium nitrate, 15 parts of sodium benzoate, 10 parts of sulfur and three parts of water had an excellent velocity-pressure ratio, that is, a relatively slow rise in pressure per unit time as indicated on a pressure-time curve similar to that shown in Figure I.

WHAT I CLAIM IS:-

1. A gas generating composition for producing controlled gas pressures which

comprises a substantially homogenous mixture of
(a) an oxygen-containing oxidizing agent, 82.5-30% by weight.
(b) an organic carboxylic acid or oxidizable derivative thereof as hereindefined, 14.5-45% by weight, and
(c) water, 25-1.0% by weight.

2. A composition according to claim 1, wherein the oxidizing agent is an alkali metal or ammonium perchlorate and the organic carboxylic acid or oxidizable derivative thereof is an aromatic carboxylic acid or alkali metal or ammonium salt thereof.

3. A composition according to claim 2, wherein the oxidizing agent is potassium perchlorate and the organic carboxylic acid or oxidizable derivative thereof is sodium benzoate.

4. A composition according to claim 1, which comprises 80-50% by weight of potassium perchlorate.

5. A composition according to claim 1, which comprises substantially 75 parts of potassium nitrate, substantially 15 parts of sodium benzoate, substantially 10 parts of sulfur and substantially three parts of water.

6. A composition according to any one of the preceding claims, which comprises from 20 to 50 per cent by weight of the composition claimed therein admixed with from 80 to 50 per cent by weight of the components of black powder.

7. A composition according to claim 6, which comprises 45 parts of potassium nitrate, nine parts of charcoal, six parts of sulfur, 19 parts of potassium perchlorate, 11 parts of sodium benzoate, six parts of dicyanamide and from one to four parts of water.

8. A process for preparing a composition according to any one of claims 1 to 5, which comprises intimately mixing the oxygen-containing oxidizing component with the organic carboxylic acid or oxidizable derivative thereof in the presence of excess water, and reducing the water to a range of 1.0 to 25 per cent by weight.

9. A process according to claim 8, in which the components for black powder are included in the mixture and the water content of the mixture is reduced to from 0.6 to 6.0 per cent by weight.

10. A process for preparing a gas generating composition substantially as herein described with reference to the Examples.

11. A gas generating composition when prepared by the process according to any one of claims 8 to 10.

12. A gas generating composition substantially as herein described with reference to the Examples.

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1601392 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIGURE I